

More generally we may obtain

$$(82.) \int_1^{\infty} \frac{x^{2r+1} + a^{2r+1}}{x^{2r+1} + a^{2r+1}} \frac{dx}{\sqrt{x^r - 1}}. \quad (83.) \int_0^{\pi} \frac{\cos r\theta \cdot d\theta}{1 + a^r \cos^r \theta}.$$

$$(84.) \int_0^{\pi} d\theta \log_e (1 + a^r \cos^r \theta). \quad (85.) \int_0^{\pi} \frac{d\theta \log_e (1 + a^r \cos^r \theta)}{1 + 2m \cos \theta + m^r}.$$

and many others.

II. "On the Reversal of the Lines of Metallic Vapours." By G. D. LIVEING, M.A., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. No. I.

Since the celebrated paper by Kirchhoff, "On the relation between the radiating and absorbing powers of different bodies for light and heat," in which he detailed the remarkable experiments of reversing the lines of lithium and sodium by sunlight and by the vapours of those metals in the flame of a Bunsen's burner, and mentioned the reversal of the brighter lines of potassium, calcium, strontium and barium when the deflagration of the chlorates with milk-sugar was used instead of the flame of a Bunsen's burner, further researches in the same direction have been made by Cornu, Lockyer, and Roberts. The method adopted by Cornu, which had been previously used by Foucault, is one of great ingenuity, dependent upon so arranging the electric arc that the continuous spectrum of the intensely heated poles is examined through an atmosphere of the metallic vapours volatilized around them. By this means Cornu succeeded in reversing several lines in the spectra of the following metals in addition to those above-mentioned, viz., thallium, lead, silver, aluminum, magnesium, cadmium, zinc, and copper. He observed that in general the reversal began with the least refrangible of a group of lines, and gradually extended to the more refrangible lines of the group; and he drew the conclusion that a very thin layer of vapour was sufficient for the reversal. It may be noted that in almost every case the lines seen by him to be reversed were the more highly refrangible of the lines characteristic of each metal, confirming generally the opinion expressed by Stokes in a letter to Lockyer in the Proceedings of the Royal Society for 1876, in which he introduces for the first time the idea of the persistency of different rays with reference to temperature.

The method adopted by Lockyer in the first instance was to view the electric arc through the vapours of the metals volatilized in a stream of hydrogen in a horizontal iron tube.

The iron tube had its ends covered with glass plates, and was heated in a furnace supplied with charcoal. By this means he did not succeed in observing any new reversal of bright lines, but he noticed an unknown absorption line which sometimes appeared when zinc was experimented on. He confirmed, however, the channelled-space absorption spectra observed by Roscoe and Schuster, in the cases of potassium and sodium, and recoded channelled-space spectra in the case of antimony, phosphorus (?), sulphur (previously observed by Salet) and arsenic (probably). "As the temperature employed for the volatilization of the metals did not exceed bright redness, or that at which cast-iron readily melts, the range of metals examined was necessarily limited; and in order to extend these observations to the less fusible metals, as well as to ascertain whether the spectra of those volatilized at the lower temperature would be modified by the application of a greater degree of heat," a new series of experiments were undertaken by Lockyer and Roberts, in which the combined action of a charcoal furnace and the oxy-hydrogen blowpipe was employed. By this means they obtained no new reversal of a metallic line, but they observed channelled-space spectra in the cases of silver, manganese, chromium, and bismuth. They observed, however, that the metal thallium gave the characteristic *bright green* line, the light of the arc not being reversed.

In the above-mentioned experiments the coolness of the ends of the tube, which acted as condensers of the metallic vapours, and the inequality of density and temperatures necessarily produced by the maintenance of a current of hydrogen in the tube, appear to us to account for the complication and uncertainty of the results of the observations.

In order to examine the reversal of the spectra of metallic vapours, we find it more satisfactory to observe the absorptive effect produced on the continuous spectrum emitted by the sides and end of the tube in which the volatilization takes place. For this purpose we find it convenient to use iron tubes about half-an-inch in internal diameter, and about 27 inches long, closed at one end, thoroughly cleaned inside, and coated on the outside with borax, or with a mixture of plumbago and fireclay. These tubes are inserted in a nearly vertical position in a furnace fed with Welsh coal, which will heat about 10 inches of the tube to about a welding heat, and we observe through the upper open end of the tube, either with or without, a cover of glass or mica. To exclude oxygen, and avoid as much as possible variations of temperature, we introduce hydrogen in a gentle stream by a narrow tube into the upper part only of the iron tube, so that the hydrogen floats on the surface of the metallic vapour without producing convection currents in it. By varying the length of the small tube conveying the hydrogen, we are able to determine the height in the tube to which the

metallic vapour reaches, and to prevent further displacement of the vapour, and thus to maintain different lengths of the iron tube full of metallic vapour at a comparatively constant temperature for considerable periods of time.

By this means the following observations have been made up to the present time.

The first metal experimented on was thallium, one of the most volatile of metals. On inserting some pieces into the hot tube, we had at first great difficulty in avoiding oxidation at the upper surface, and we observed no reversal. However, after arranging the current of hydrogen so as to keep the tube free from air, but without any rapid movement of the gas, we succeeded in seeing the characteristic line reversed, and maintained it so for a considerable time.

The metal indium, closely allied in its behaviour and volatility to thallium, was next examined, and although the amount of this metal at our disposal was not large, we observed the bright blue line reversed. This was most plainly visible when that portion of the vapour which was nearest to the sides of the tube was looked through.

We had great difficulty in preventing the oxidation of magnesium in the tube, and in using tubes wider than half-an-inch did not succeed in getting any reversal, but with half-inch tubes the *b* lines were clearly and sharply reversed, also some dark lines, not measured, were seen in the blue. The sharpness of these lines depended on the regulation of the hydrogen current, by which we could cool the upper stratum of vapour at will.

A piece of metallic lithium was introduced, and gave no results. Sodium was next added in the same tube, and this did not bring out the reversal of the lithium lines. Similarly, chloride of lithium and metallic sodium, introduced together, gave no better results. To a tube containing potassium vapour, some lithium chloride was added, but no lithium line appeared. On adding metallic sodium to this atmosphere, and more lithium chloride, the bright-red lithium line appeared sharply reversed, and remained well defined for a long time. It is worthy of observation that the lithium line was only reversed in a mixture of the vapours of potassium and sodium, and it seems highly probable that a very slightly volatile vapour may be diffused in an atmosphere of a more volatile metal, so as to secure a sufficient depth of vapour to produce a sensible absorption. This would be analogous to well-known actions which take place in the attempt to separate organic bodies of very different boiling points by distillation, where a substance of high boiling point is always carried over, in considerable quantity, with the vapour of a body boiling at a much lower temperature. It is a matter for future investigation how far chemical interactions taking place in a mixture of metallic vapours affect the volatility of a third body, and what relation, if any, this may have to

such phenomena as the increased fusibility of mixtures of salts of potassium and sodium, and the well-known fluidity of the alloy of those metals.

As we have had occasion to use sodium and potassium in our tubes, we have had opportunities of observing the absorption spectra of these metals, and we find that there is a great deal yet to be observed in regard to these spectra. Up to the present time, we have not observed any of the appearances noted by Lockyer, "On a new class of absorption phenomena," in the *Proceedings of the Royal Society*, vol. xxii, but we have repeatedly noted the channelled-space spectrum of sodium described by Roscoe and Schuster in the same volume of the *Proceedings*. We observed in our tubes no channelled-space absorption by potassium, but continuous absorption in the red, and one narrow absorption band, with a wave-length of about 5,730, not corresponding with any bright line of that metal.

With reference to the absorption spectrum of sodium vapour, we may remark that it is by no means so simple as has been generally represented. The fact that the vapour of sodium in a flame shows only the reversal of the D lines, while the vapour, volatilized in tubes, shows a channelled-space absorption corresponding to no known emission spectrum, appears to be part of a gradational variation of the absorption spectrum, which may be induced with perfect regularity. Experiments with sodium, carried out in the way we have described, exhibit the following succession of appearances, as the amount of vapour is gradually diminished, commencing from the appearance when the tube is full of the vapour of sodium, part of it condensing in the cooler portion of the tube, and some being carried out by the slow current of hydrogen. During this stage, although the lower part of the tube is at a white heat, we have always noticed, as long as the cool current of hydrogen displaced metallic vapour, that, on looking down the tube, it appeared perfectly dark. The first appearance of luminosity is of a purple tint, and, with the spectroscope, appears as a faint blue band, commencing with a wave-length of about 4,500, and fading away into the violet. Next appears a narrow band in the green, with a maximum of light, with a wave-length of about 5,420, diminishing in brightness so rapidly on either side as to appear like a bright line. This green band gradually widens, and is then seen to be divided by a dark band, with a wave-length of about 5,510. Red light next appears, and between the red and green light is an enormous extension of the D absorption line, while a still broader dark space intervenes between the green and the blue light. The dark line in the green (wave-length about 5,510) now becomes more sharply defined. This line appears to have been observed by Roscoe and Schuster, and regarded by them as coinciding with the double sodium line next in strength to the D lines, but it is considerably more refran-

gible than that double line. In the next stage, the channelled-space spectrum comes out in the dark space between the green and blue, and finally, in the red. Gradually the light extends, the channels disappear, the D line absorption narrows, but still the dark line in the green is plainly discernible. Lastly, there is only D lines absorption. So far as we can judge, the blue and the streak of green light at first observed are due to luminosity of the vapour itself, where it is somewhat cooled, the later stages being mixed phenomena of absorption and emission.

As the absorption line, with wave-length about 5,510, which we may call for shortness the second absorption line of sodium, has not been distinctly recorded by other observers, we have endeavoured to trace it under somewhat different conditions from that of the vapour volatilized in white hot iron tubes. This absorption-line is easily seen when a gas flame is observed through a horizontal glass tube, about three inches long, containing sodium volatilized in the middle of the tube by the heat of a Bunsen's burner, and equally well whether the tube contains hydrogen or nitrogen besides sodium. We have also observed the same absorption line when a piece of commercial magnesium ribbon (which always contains sodium) is ignited in a horizontal position, so that the metal melts and produces an elongated flame. It is of some interest to note that absorption lines of about this wave-length, in the solar spectrum, are given by Kirchhoff and Ångström not corresponding with emission lines of known elementary bodies.

When potassium vapour is observed, whether in the iron tube or in a glass tube, an absorption line is seen, with a wave-length of about 5,730, which is more refrangible than the yellow double emission line of potassium, and does not correspond to any known bright line of that metal.

We reserve, for a future communication, the discussion of the identity or non-identity of these absorption lines with lines in the solar spectrum and the inferences which may be drawn from such determination.

The method of observation we have described may be used to observe emission spectra as well as absorption spectra, for if the closed end of the tube be placed against the bars of the furnace so as to be relatively cooler than the middle of the tube, the light emitted by the vapours in the hottest part is more intense than that emitted by the bottom of the tube. This succeeds admirably with sodium, but we have not specially observed it with other vapours.